Supporting Information

Cobalt-catalyzed, directed C-H functionalization/annulation of phenylglycinol derivatives with alkynes

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General considerations

Reactions were performed using standard glassware or were run in 4 mL vials with PTFE/Liner screw caps and 30 mL vials using w/polyseal screw caps. Reactions were heated using Chemglass aluminium reaction blocks. Column chromatography was performed using Kieselgel silicagel (35 -70 and 60 - 200 μm). Thin layer chromatography (TLC) was performed on silica gel using Merck TLC Silica gel 60 F254 Aluminum sheets and was visualized by UV lamp, staining with KMnO4. 

1H, 13C, 19F and 2D-NMR spectra were recorded on 400 MHz Bruker spectrometer using residual solvent peak as a reference. Compounds for HRMS were analyzed by positive mode electrospray ionization (ESI) using Waters Synapt G2-Si mass spectrometer. HPLC data were obtained using Waters Alliance 2695 HPLC system with a Phenomenex Lux Amylose-1 (4.6 x 150 mm) or Chiralpac IC-1 (4.6 x 250 mm) column (conditions specified on attached HPLC chromatograms). IR spectra were obtained using a Shimadzu IR Prestige-21 FT-IR spectrometer. Optical rotations were measured at 20 °C on a Rudolph Research Analytical Autopol VI Polarimeter, cell length 50 mm, using solvent and concentration stated, at 589 nm. All procedures were performed under ambient air unless otherwise noted. Reagents and starting materials were obtained from commercial sources and used without further purification unless otherwise noted.
Cobalt-catalyzed sp² C-H functionalization

1. Optimization of cobalt-catalyzed sp² C-H functionalization

3.1. Oxidant

**General procedure for oxidant optimization experiments.**

A 4 mL vial with a screw cap (PTFE/Liner) was charged with \( N-(2-((\text{tert}-\text{butyldimethylsilyl})\text{oxy})-1\text{-phenylethyl})\text{picolinamide} (35.6 \text{ mg}, 0.1 \text{ mmol}), \) oxidant (0.2 – 0.3 mmol, 2 – 3 equiv), \( \text{NaOPiv} \) (24.8 mg, 0.2 mmol, 2 equiv), \( \text{Co(OAc)}_2 \) ( 3.5 mg, 0.02 mmol, 20 mol%), 3,3-dimethyl-1-butyne (37 \( \mu \)L, 0.3 mmol, 3 equiv), and \( \text{MeOH} \) (1.0 mL). Resulting mixture was heated at 80 °C for 16 h, cooled to room temperature and analyzed by TLC (hexanes/EtOAc 4:1). To reaction mixture \( \text{Ph}_3\text{CH} \) (24.4 mg, 0.1 mmol, 1 equiv) was added, mixture was diluted with dist. \( \text{H}_2\text{O} \) (1.5 mL) and extracted with \( \text{EtOAc} \) (3 x 1.5 mL). Combined organic phase was separated, dried over anh. \( \text{Na}_2\text{SO}_4 \), filtered, evaporated. The residue was dissolved in \( \text{CDCl}_3 \) and analyzed by \(^1\text{H}-\text{NMR} \) spectroscopy.

![Chemical structure](image)

**Table S1. Oxidant optimization experiments**

| Entry | Oxidant (equiv) | Substrate : Product ratio | NMR yield, %
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>AgOAc (2)</td>
<td>17:1</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>AgOPiv (2)</td>
<td>1:0</td>
<td>ND</td>
</tr>
<tr>
<td>3</td>
<td>MnO₂ (2)</td>
<td>11:1</td>
<td>4</td>
</tr>
<tr>
<td>4</td>
<td>Mn(acac)₃ (2)</td>
<td>1:0</td>
<td>ND</td>
</tr>
<tr>
<td>5</td>
<td>Mn(OAc)₂·4H₂O (2)</td>
<td>19:1</td>
<td>5</td>
</tr>
<tr>
<td>6</td>
<td>Mn(OAc)₃·2H₂O (2)</td>
<td>7:1</td>
<td>12</td>
</tr>
<tr>
<td>7</td>
<td>Mn(OAc)₃·2H₂O (3)</td>
<td>7:1</td>
<td>12</td>
</tr>
<tr>
<td>8</td>
<td>O₂</td>
<td>1:0</td>
<td>ND</td>
</tr>
<tr>
<td>9</td>
<td>Mn(OAc)₃·2H₂O (2)/O₂</td>
<td>5.3:1</td>
<td>16</td>
</tr>
<tr>
<td>10</td>
<td>w/o oxidant</td>
<td>1:0</td>
<td>ND</td>
</tr>
</tbody>
</table>

* NMR yield using triphenylmethane as an internal standard. ND – not determined.
3.2. Base

General procedure for base optimization experiments.
A 4 mL vial with a screw cap (PTFE/Liner) was charged with N-(2-((tert-butyldimethylsilyl)oxy)-1-phenylethyl)picolinamide (35.6 mg, 0.1 mmol), Mn(OAc)₃ · 2 H₂O (53.6 mg, 2 equiv), base (0.12 - 0.3 mmol, 1.2 - 3 equiv), Co(OAc)₂ (3.5 mg, 0.02 mmol, 20 mol%), 3,3-dimethyl-1-butyne (37 µL, 0.3 mmol, 3 equiv), and MeOH (1.0 mL). Vial was purged with O₂ for 1 minute and the resulting mixture was heated at 80 °C for 16 h, cooled to room temperature and analyzed by TLC (hexanes/EtOAc 4:1). To reaction mixture Ph₃CH (24.4 mg, 0.1 mmol, 1 equiv) was added, mixture was diluted with dist. H₂O (1.5 mL) and extracted with EtOAc (3 x 1.5 mL). Combined organic phase was separated, dried over anh. Na₂SO₄, filtered, evaporated. The residue was dissolved in CDCl₃ and analyzed by ¹H-NMR spectroscopy.

Table S2. Base optimization experiments

<table>
<thead>
<tr>
<th>Entry</th>
<th>Base (equiv)</th>
<th>Substrate : Product ratio</th>
<th>NMR yield, %&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NaOAc (2)</td>
<td>7.3:1</td>
<td>12</td>
</tr>
<tr>
<td>2</td>
<td>PhCOONa (2)</td>
<td>2.8:1</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>AdCOONa (2)</td>
<td>3.4:1</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>NaOPiv (2)</td>
<td>5.3:1</td>
<td>16</td>
</tr>
<tr>
<td>5</td>
<td>NaOPiv (1.2)</td>
<td>2.5:1</td>
<td>28</td>
</tr>
<tr>
<td>6</td>
<td>NaOPiv (3)</td>
<td>2.6:1</td>
<td>25</td>
</tr>
<tr>
<td>7</td>
<td>w/o base</td>
<td>4.5:1</td>
<td>16</td>
</tr>
</tbody>
</table>

<sup>a</sup>NMR yield using triphenylmethane as an internal standard.

3.3. Solvent

General procedure for solvent optimization experiments.
A 4 mL vial with a screw cap (PTFE/Liner) was charged with N-(2-((tert-butyldimethylsilyl)oxy)-1-phenylethyl)picolinamide (35.6 mg, 0.1 mmol), Mn(OAc)₃ · 2 H₂O (53.6 mg, 2 equiv), NaOPiv (14.9 mg, 0.12 mmol, 1.2 equiv), Co(OAc)₂ (3.5 mg, 0.02 mmol, 20 mol%), 3,3-dimethyl-1-butyne (37 µL, 0.3 mmol, 3 equiv), and solvent (1.0 mL). Vial was purged with O₂ for 1 minute and
the resulting mixture was heated at 80 °C for 16 h, cooled to room temperature and analyzed by TLC (hexanes/EtOAc 4:1). To reaction mixture Ph₃CH (24.4 mg, 0.1 mmol, 1 equiv) was added, mixture was diluted with dist. H₂O (1.5 mL) and extracted with EtOAc (3 x 1.5 mL). Combined organic phase was separated, dried over anh. Na₂SO₄, filtered, evaporated. The residue was dissolved in CDCl₃ and analyzed by ¹H-NMR spectroscopy.

![Diagram](image)

**Table S3.** Solvent optimization experiments

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Substrate : Product ratio</th>
<th>NMR yield, %&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MeOH</td>
<td>2.5:1</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>EtOH</td>
<td>98:1</td>
<td>1</td>
</tr>
<tr>
<td>3</td>
<td>TFE</td>
<td>6.7:1</td>
<td>13</td>
</tr>
<tr>
<td>4</td>
<td>DCE</td>
<td>32:1</td>
<td>3</td>
</tr>
<tr>
<td>5</td>
<td>PhCl</td>
<td>32:1</td>
<td>3</td>
</tr>
<tr>
<td>6</td>
<td>Toluene</td>
<td>17.6:1</td>
<td>5</td>
</tr>
</tbody>
</table>

<sup>a</sup> NMR yield using triphenylmethane as an internal standard.

### 3.4. Catalyst

**General procedure for catalyst optimization experiments.**

A 4 mL vial with a screw cap (PTFE/Liner) was charged with N-(2-((tert-butyldimethylsilyl)oxy)-1-phenylethyl)picolinamide (35.6 mg, 0.1 mmol), Mn(OAc)₃ · 2 H₂O (53.6 mg, 2 equiv), NaOPiv (14.9 mg, 0.12 mmol, 1.2 equiv), catalyst (0.01 - 0.02 mmol, 10 - 20 mol%), 3,3-dimethyl-1-butyne (37 µL, 0.3 mmol, 3 equiv), and MeOH (1.0 mL). Vial was purged with O₂ for 1 minute and the resulting mixture was heated at 80 °C for 16 h, cooled to room temperature and analyzed by TLC (hexanes/EtOAc 4:1). To reaction mixture Ph₃CH (24.4 mg, 0.1 mmol, 1 equiv) was added, mixture was diluted with dist. H₂O (1.5 mL) and extracted with EtOAc (3 x 1.5 mL). Combined organic phase was separated, dried over anh. Na₂SO₄, filtered, evaporated. The residue was dissolved in CDCl₃ and analyzed by ¹H-NMR spectroscopy.
### Table S4. Catalyst optimization experiments

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol%)</th>
<th>Substrate : Product ratio</th>
<th>NMR yield, %a</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co(OAc)₂ (20)</td>
<td>2.5:1</td>
<td>28</td>
</tr>
<tr>
<td>2</td>
<td>Co(acac)₂ (20)</td>
<td>2.3:1</td>
<td>30</td>
</tr>
<tr>
<td>3</td>
<td>CoCl₂ (20)</td>
<td>&gt;10:1</td>
<td>ND</td>
</tr>
<tr>
<td>4</td>
<td>Co(acac)₃ (20)</td>
<td>5:1</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>Co(dpm)₂ (20)</td>
<td>1:13.7</td>
<td>82</td>
</tr>
<tr>
<td>6b</td>
<td>Co(dpm)₂ (20)</td>
<td>1:16.8</td>
<td>84</td>
</tr>
<tr>
<td>7c</td>
<td>Co(dpm)₂ (20)</td>
<td>1:1</td>
<td>49</td>
</tr>
<tr>
<td>8</td>
<td>Co(dpm)₂ (10)</td>
<td>1:1.4</td>
<td>57</td>
</tr>
<tr>
<td>9</td>
<td>Cu(OAc)₂ (20)</td>
<td>1:0</td>
<td>ND</td>
</tr>
<tr>
<td>10</td>
<td>w/o catalyst</td>
<td>1:0</td>
<td>ND</td>
</tr>
</tbody>
</table>

a NMR yield using triphenylmethane as an internal standard. b Time: 24 h. c Without purging with O₂.

**Note!** Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(II) (Co(dpm)₂) can be used commercial (Alfa Aesar, CAS: 13986-53-3) or self-made (by procedure written below).

**Bis(2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(II)**

Co(NO₃)₂ · 6 H₂O (1.61 g, 5.53 mmol, 1 equiv) and 2,2,6,6-tetramethyl-3,5-heptanedione (2.36 mL, 11.29 mmol, 2.04 equiv) were dissolved in MeOH (15 mL), then 2 M NaOHₐq (443 mg, 11.07 mmol, 15 mL dist. H₂O) was added dropwise (formation of pink precipitate) and the resulting mixture was heated at 80 °C for 2 h. Mixture was cooled to room temperature, the pink precipitate was filtered off. Then precipitate was dissolved in Et₂O (10 mL), filtered, filtrate was evaporated and dried under reduced pressure to give 1.5 g (64%) of bis(2,2,6,6-tetramethyl-3,5-heptanedionato)cobalt(II) as a pink powder, mp 142-144 °C (Et₂O).

#### 3.5. Temperature

**General procedure for temperature optimization experiments.**

A 4 mL vial with a screw cap (PTFE/Liner) was charged with N-(2-((tert-butyldimethylsilyl)oxy)-1-phenylethyl)picolinamide (35.6 mg, 0.1 mmol), Mn(OAc)₃ · 2 H₂O (53.6 mg, 2 equiv), NaOPiv (14.9 mg, 0.12 mmol, 1.2 equiv), Co(dpm)₂ (8.5 mg, 0.02 mmol, 20 mol%), 3,3-dimethyl-1-butyne (37 µL, 0.3 mmol, 3 equiv), and MeOH (1.0 mL). Vial was purged with O₂ for 1 minute and the
resulting mixture was heated at corresponding temperature for 16 h, cooled to room temperature and analyzed by TLC (hexanes/EtOAc 4:1). To reaction mixture Ph$_3$CH (24.4 mg, 0.1 mmol, 1 equiv) was added, mixture was diluted with dist. H$_2$O (1.5 mL) and extracted with EtOAc (3 x 1.5 mL). Combined organic phase was separated, dried over anh. Na$_2$SO$_4$, filtered, evaporated. The residue was dissolved in CDCl$_3$ and analyzed by $^1$H-NMR spectroscopy.

![Chemical structure](image)

**Table S5. Temperature optimization experiments**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Temperature, °C</th>
<th>Substrate : Product ratio</th>
<th>NMR yield, %$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>1:13.7</td>
<td>82</td>
</tr>
<tr>
<td>2</td>
<td>60</td>
<td>2.3:1</td>
<td>29</td>
</tr>
</tbody>
</table>

$^a$NMR yield using triphenylmethane as an internal standard.
2. Cobalt-catalyzed sp² C-H alkenylation using literature procedure for benzamides

We tested the reported reaction conditions for cobalt catalyzed benzamide sp² C-H alkenylation with alkynes using our model substrate – N-(2-((tert-butyldimethylsilyl)oxy)-1-phenylethyl)-picolinamide.

Note! This substrate was not tested by Carretero, Cui and Daugulis groups.

Table S6. Control reactions using literature procedures

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>NMR yield, %[^a]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Picolinamide 1a (0.1 mmol, 1 equiv), phenylacetylene (1.5 equiv), Co(OAc)₂ (0.015 mmol, 15 mol%), NaOAc (0.15 mmol, 1.5 equiv), EtOH (1 mL), O₂, 100 °C, 16h</td>
<td>NR</td>
<td>¹</td>
</tr>
<tr>
<td>2</td>
<td>Picolinamide 1a (0.1 mmol, 1 equiv), phenylacetylene (1.5 equiv), Co(OAc)₂ (0.015 mmol, 15 mol%), NaOAc (0.15 mmol, 1.5 equiv), 1,4-Dioxane (1 mL), O₂, 100 °C, 2.5h</td>
<td>NR</td>
<td>²</td>
</tr>
<tr>
<td>3</td>
<td>Picolinamide 1a (0.1 mmol, 1 equiv), phenylacetylene (1.5 equiv), Co(OAc)₂·4H₂O (0.05 mmol, 50 mol%), KPF₆ (0.05 equiv, 50 mol%), PEG-400, O₂, 140 °C, 16h</td>
<td>33:13:2</td>
<td>³</td>
</tr>
<tr>
<td>4</td>
<td>Picolinamide 1a (0.1 mmol, 1 equiv), phenylacetylene (1.5 equiv), Co(OAc)₂·4H₂O (0.1 mmol, 1 equiv), NaOPiv (0.2 mmol, 2 equiv), Mn(OAc)₂ (0.2 mmol, 2 equiv), air, TFE (1 mL), 100 °C, 16h</td>
<td>98:2:0</td>
<td>³</td>
</tr>
</tbody>
</table>

[^a]: NMR yield using triphenylmethane as an internal standard.

Mehanistic considerations

Cyclization of picolinamide 1s

Reactions were performed using general procedure for cobalt-catalyzed $sp^2$ C-H alkenylation/cyclization.

![Chemical reaction diagram](attachment:chemical_diagram.png)

**Table S7. Cyclization of picolinamide 1d**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>NMR yield 2af, %$^a$</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>w/o Co(dpm)$_2$</td>
<td>0</td>
<td>No reaction</td>
</tr>
<tr>
<td>2</td>
<td>Standard</td>
<td>0</td>
<td>Formation of byproducts</td>
</tr>
</tbody>
</table>

$^a$NMR yield using triphenylmethane as an internal standard.
NMR spectra

$^1$H NMR (400 MHz, CDCl$_3$)

![NMR spectrum image]
$^{13}\text{C (H)}$ NMR (100 MHz, CDCl$_3$)

![Diagram of a chemical structure]

5h
$^1$H NMR (400 MHz, CDCl$_3$)

![NMR Spectrogram]
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

5j
$^{13}$C$\{H\}$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

5k
$^{13}\text{C} \{\text{H}\}$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)
$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

5m
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)

5m

\[ \text{Chemical Shifts:} \quad 171.39, 163.91, 157.54, 148.42, 137.40, 129.94, 128.81, 128.55, 122.46, 116.82, 94.47 \]

\[ \text{Chemical Shifts:} \quad 77.48 \text{ CDCl}_3, 77.16 \text{ CDCl}_3, 56.20, 52.92 \]
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

5p

(Chemical structure and NMR spectrum image)
$^{13}\text{C}\{\text{H}\} \text{ NMR (100 MHz, CDCl}_3\}$

5p

![NMR Spectrum]
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C\{H\} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

[Chemical structure diagram]

[Spectrum image]
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

[Spectrum Image]
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{\(\text{H}\)} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}\text{C}\{\text{H}\} \text{ NMR (100 MHz, CDCl}_3\}$

\[ \text{Chemical Structure} \]

$^{13}\text{C}\{\text{H}\} \text{ NMR (100 MHz, CDCl}_3\}$
$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
\(^1\)H NMR (400 MHz, CDCl\(_3\))
$^{13}$C{\text{H}} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

[Chemical structure and spectrum image]
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
2D (COSY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)

2D-NOESY

2aa

Hₐ, H₉, H₈, H₇, H₆, H₅, H₄, H₃, H₂, H₁

f₁ (ppm)

f₂ (ppm)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C\{H\} NMR (100 MHz, CDCl$_3$)
2D (COSY) NMR (400 MHz, CDCl$_3$)
2D (NOESY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

2da

[Chemical Structure Image]
$^{13}$C\{H\} NMR (100 MHz, CDCl$_3$)

\[ \text{2da} \]

\[
\begin{array}{cccccccccccc}
171.02 & 153.59 & 149.01 & 136.98 & 133.77 & 128.69 & 126.69 & 126.68 & 125.79 & 125.37 & 118.12 & 96.32
\end{array}
\]

\[
\begin{array}{cccccccccccc}
136.98 & 132.77 & 131.57 & 128.01 & 126.08 & 125.79 & 125.37 & 118.12
\end{array}
\]

\[
\begin{array}{cccccccccccc}
77.48 & 77.16 & 76.84 & 58.45 & 55.33 & 36.66 & 30.98
\end{array}
\]

\[
\begin{array}{cccccccccccc}
\end{array}
\]

\[
\begin{array}{cccccccccccc}
20 & 190 & 180 & 170 & 160 & 150 & 140 & 130 & 120 & 110 & 100 & 90 & 80 & 70 & 60 & 50 & 40 & 30 & 20 & 10 & 0
\end{array}
\]
2D (COSY) NMR (400 MHz, CDCl$_3$)
2D (NOESY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
2D (COSY) NMR (400 MHz, CDCl₃)

2D-COSY

2ea
2D (NOESY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)

2fa
$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl$_3$)

![NMR spectrum image](image-url)
2D (COSY) NMR (400 MHz, CDCl$_3$)
2D (NOESY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl$_3$)
2D (COSY) NMR (400 MHz, CDCl$_3$)

2D-COSY
2D (NOESY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)

![13C NMR spectrum of compound 2ha](image)
2D (COSY) NMR (400 MHz, CDCl$_3$)
2D (NOESY) NMR (400 MHz, CDCl$_3$)
2D (NOESY) NMR (400 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
2D (COSY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)

[Diagram of 2D-NOESY NMR spectrum with chemical structure of compound 2ia]
2D (NOESY) NMR (400 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)

![NMR spectrum of compound 2ja](image-url)
\(^{13}\text{C}\{\text{H}\} \text{ NMR (100 MHz, CDCl}_3\)
2D (COSY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
2D (COSY) NMR (400 MHz, CDCl$_3$)
2D (NOESY) NMR (400 MHz, CDCl₃)

2D-NOESY

Me

OTES

2ka
2D (NOESY) NMR (400 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)
$^{13}$C\{H\} NMR (100 MHz, CDCl$_3$)
2D (COSY) NMR (400 MHz, CDCl$_3$)
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2D (NOESY) NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C\{(H\) NMR (100 MHz, CDCl$_3$)

\begin{align*}
2\text{ma} & \quad 171.33 \\
& \quad 157.04 \\
& \quad 153.76 \\
& \quad 149.97 \\
& \quad 150.07 \\
& \quad 149.37 \\
& \quad 136.78 \\
& \quad 132.92 \\
& \quad 127.54 \\
& \quad 125.75 \\
& \quad 118.15 \\
& \quad 114.8 \\
& \quad 113.26 \\
& \quad 94.59 \\
& \quad 77.48 \text{CDCl}_3 \\
& \quad 77.36 \text{CDCl}_3 \\
& \quad 76.84 \text{CDCl}_3 \\
& \quad 62.42 \\
& \quad 60.31 \\
& \quad 56.01 \\
& \quad 36.76 \\
& \quad 30.96 \\
& \quad 26.00 \\
& \quad 18.43 \\
& \quad -5.39
\end{align*}
2D (COSY) NMR (400 MHz, CDCl$_3$)
2D (NOESY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)

2D-NOESY

2ma

H₂

H₂

H₂

H₂

H₂
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{\text{H}}$ NMR (100 MHz, CDCl$_3$)
2D (COSY) NMR (400 MHz, CDCl$_3$)
2D (NOESY) NMR (400 MHz, CDCl$_3$)
2D (NOESY) NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C-H NMR (100 MHz, CDCl$_3$)
2D (COSY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)

F

OTBS

20a

\text{2D-NOESY}
2D (NOESY) NMR (400 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
2D (COSY) NMR (400 MHz, CDCl$_3$)
2D (NOESY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}\text{C}\{\text{H}\}$ NMR (100 MHz, CDCl$_3$)

Major regiosomer 2qa

Minor regiosomer
2D (COSY) NMR (400 MHz, CDCl₃)

2D-COSY, Mixture of isomers

Major regioisomer

2qa
2D (NOESY) NMR (400 MHz, CDCl₃)

2D-NOESY, Mixture of isomers

Major regioisomer

2qa
2D (NOESY) NMR (400 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl₃)
$^{13}\text{C}(\text{H})$ NMR (100 MHz, CDCl$_3$)
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2D (NOESY) NMR (400 MHz, CDCl$_3$)
2D (NOESY) NMR (400 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)
2D (COSY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)
$^{1}$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)

C$_2$D$_2$Cl$_4$: 65°C Temperature
$^{13}$C{H} NMR (100 MHz, C$_2$D$_2$Cl$_4$)

2ac
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)

C$_2$D$_2$Cl$_4$ 65°C

C$_2$D$_2$Cl$_4$ 250°C
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)

C$_2$D$_2$Cl$_4$: 65°C Temperature
$^{13}$C{H} NMR (100 MHz, C$_2$D$_2$Cl$_4$)

| f$_1$ (ppm) | 168.48  | 166.82  | 153.69  | 152.87  | 154.82  | 133.31  | 131.69  | 127.15  | 127.69  | 126.89  | 126.69  | 124.10  | 123.72  | 74.06  |
|------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
|            | 136.64  | 135.74  | 134.42  | 133.31  | 133.11  | 127.73  | 127.69  | 124.84  | 124.60  | 124.40  | 124.20  | 123.72  | 122.72  | 73.18  | 63.12  |
|            |         |         |         |         |         |         |         |         |         |         |         |         |         |         | 58.57  |
|            |         |         |         |         |         |         |         |         |         |         |         |         |         |         | 58.66  |
|            |         |         |         |         |         |         |         |         |         |         |         |         |         |         | 57.96  |
|            |         |         |         |         |         |         |         |         |         |         |         |         |         |         | 56.48  |

*2ad*
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)

C$_2$D$_2$Cl$_4$ 65°C

C$_2$D$_2$Cl$_4$ 25°C
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)

2ae

C$_2$D$_2$Cl$_4$: 65°C Temperature

S-162
$^{13}$C{H} NMR (100 MHz, C$_2$D$_2$Cl$_4$)
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C{H} NMR (100 MHz, C$_2$D$_2$Cl$_4$)
2D (COSY) NMR (400 MHz, C₂D₂Cl₄)
2D (NOESY) NMR (400 MHz, C₂D₂Cl₄)
2D (COSY) NMR (400 MHz, C₆D₅Cl₄)
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)

$C_2D_2Cl_4$ 650C

$C_2D_2Cl_4$ 250C

S-169
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)
$^{13}$C{H} NMR (100 MHz, C$_2$D$_2$Cl$_4$)
2D (COSY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)
2D (NOESY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)
\[ ^1H \text{NMR (400 MHz, C}_2\text{D}_2\text{Cl}_4) \]

\[ \text{C}_2\text{D}_2\text{Cl}_4 \text{ 65°C} \]

\[ \text{C}_2\text{D}_2\text{Cl}_4 \text{ 25°C} \]
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)
$^{13}$C$\{H\}$ NMR (100 MHz, C$_2$D$_2$Cl$_4$)

![Chemical Structure Image]

2ah

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2D (NOESY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)
2D (NOESY) NMR (400 MHz, C₂D₂Cl₂)
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)
$^{13}$C{H} NMR (100 MHz, C$_2$D$_2$Cl$_4$)

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2D (COSY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)
2D (NOESY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)
2D (NOESY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)

C$_2$D$_2$Cl$_4$; 65°C Temperature

2ai
$^{13}$C{H} NMR (100 MHz, C$_2$D$_2$Cl$_4$)
2D (COSY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)
2D (NOESY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)
2D (NOESY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)

2D-NOESY
Nonoe between Py and $H_a$

S-190
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)
$^{13}$C{H} NMR (100 MHz, C$_2$D$_2$Cl$_4$)
2D (COSY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)
2D (NOESY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)
2D (NOESY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)
$^{13}$C$\{H\}$ NMR (100 MHz, C$_2$D$_2$Cl$_4$)
2D (NOESY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)

2al
$^{13}$C{H} NMR (100 MHz, C$_2$D$_2$Cl$_4$)

![Chemical Structure](image)
$^1$H NMR (400 MHz, C$_2$D$_2$Cl$_4$)
$^{13}$C\{H\} NMR (100 MHz, C$_2$D$_2$Cl$_4$)
2D (COSY) NMR (400 MHz, C<sub>2</sub>D<sub>2</sub>Cl<sub>4</sub>)
2D (NOESY) NMR (400 MHz, C$_2$D$_2$Cl$_4$)
2D (NOESY) NMR (400 MHz, C\textsubscript{2}D\textsubscript{2}Cl\textsubscript{4})
$^1$H NMR (400 MHz, CDCl$_3$)
$^{13}$C\{H\} NMR (100 MHz, CDCl$_3$)

![NMR spectrum of 2an](image-url)
2D (COSY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)
2D (NOESY) NMR (400 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)

(S,S)-3an
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)

(S,S)-3an

- 169.25
- 155.54
- 148.46
- 136.93
- 135.77
- 128.19
- 127.59
- 124.05
- 77.36 CDCl$_3$
- 76.84 CDCl$_3$
- 56.40
- 60.84
- 43.59
- 29.50
- 25.95
- 18.41
- 1.38
- 5.45
2D (HSQC) NMR (100 MHz, CDCl₃)
2D (COSY) NMR (400 MHz, CDCl₃)

(S,S)-3an
$^1$H NMR (400 MHz, CDCl$_3$)

(S,S)-4an
$^{13}$C{H} NMR (100 MHz, CDCl$_3$)

(S,S)-4an

140 138 136 134 132 130 128 126 124
f$_1$ (ppm)

20 110 100 90 80 70 60 50 40 30 20 10 0
f$_1$ (ppm)
2D (HSQC) NMR (100 MHz, CDCl₃)
2D (COSY) NMR (400 MHz, CDCl₃)

(S,S)-4an
2D (NOESY) NMR (400 MHz, CDCl₃)

(S,S)-4an
2D (NOESY) NMR (400 MHz, CDCl₃)
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**Acquired By:** System

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**Lux Amylose-1(2) (4.6x150 mm)**  
Iz. 5%IPA + 95% HEX; F=1 mL/min; T=250°C

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**Lux Amylose-1(2) (4.6x150 mm)**  
5% IPA + Hex; F=1 mL/min; T=250°C

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